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Unrestricted Hartree Fock method and the level shifting technique

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Recently Saunders *et al* (1973) have developed an elegant strategy to achieve convergence in closed and restricted open-shell calculations where the traditional Roothaan method fails to reach a stationary point on the energy surface because of an unpredictable swaping of the orbitals spanning the occupied and virtual orbital spaces. This method is known as the level-shifting method. The purpose of the present note is to extend the method of open-shell SCF-MO-LCAO calculations in the unrestricted Hartree Fock formalism (Amos & Hall 1961) and to discuss some of the possible improvements in the methods of implementation of the scheme. Some of the general features of the method are also pointed out.

The first order energy change resulting from the independent variations of the α and β-spin orbitals spanning the occupied subspaces (ψ^{α}_1, $\psi_1{}^{\beta}$), onto the corresponding virtual sub-spaces ($\psi_2{}^{\alpha}$, $\psi_2{}^{\beta}$) can be shown to be equal to $\delta E^{(1)}$ where,

$$\delta E^{(1)} = \delta E_{\alpha}{}^{(1)} + \delta E_{\beta}{}^{(1)} = 2 \sum_{k} \sum_{i} (H^{\alpha}_{ki})^2 / H^{\alpha}_{kk} - H^{\alpha}_{ii} + 2 \sum_{k} \sum_{i} \frac{(H^{\beta}_{ki})^2}{H^{\beta}_{kk} - H^{\beta}_{ii}} \tag{1}$$

where H^{α} and H^{β} are the spin-polarised Hamiltonian operators in the molecular orbital basis, k sums over the occupied orbital space and i over the virtua-orbital space respectively. For a smooth energy lowering, the energy denominators in $\delta E_{\alpha}{}^{(1)}$ and $\delta E_{\beta}{}^{(1)}$ must be negative, a constraint that is easily satisfied by adding fairly large shifting parameters b_{α} and b_{β} only to the H^{α}_{ii} and H^{β}_{ii} type of matrix elements (diagonal elements in the virtual orbital block) respectively. This condition can be incorporated in the unrestricted SCF-MO-LCAO

(UHF) scheme by using the projection operator technique (Huzinaga & Arnau 1971) and H^{α} and H^{β} operators in the atomic orbital (AO basis). Thus if $F^{\alpha}{}_0$ and $F^{\beta}{}_0$ be the unshifted UHF Hamiltonians in the AO-basis, the corresponding level-shifted operator are given by—

$$\left.\begin{aligned} F^{\alpha} &= F^{\alpha}{}_0+(I-P^{\alpha})+b_{\alpha}(I-P^{\alpha}) \\ F &= F_0+(I-P^{\beta})+b_{\beta}(I-P^{\beta}) \end{aligned}\right\} \qquad (2)$$

where P^{α} and P^{β} are the one-electron density matrices corresponding to the α- and β-spin orbitals and I is the identity matrix. F^{α} and F^{β} can then be diagonalised, the output vectors C^{α} and C^{β} being used to construct the new $F^{\alpha}{}_0$ and $F^{\beta}{}_0$ matrices.

(1) To test the efficiency of the method we have performed a modified CNDO-MO type of calculations (Bhattacharyya & Chowdhury 1976) on the $^6A_{1g}$ state of $C_0F_6^{-4}$ ion which displayed random oscillations in the electronic energy in course of an ordinary Roothaan UHF calculation. The shifting parameter used is 20 eVs. The results summarised in Table 1 shows the smooth convergence achieved.

Table 1. Convergence properties of UHF and LSUHF calculations on $C_0F_6^{-4}$

Total electronic energy E_{LSUHF}.	Total electronic energy E_{UHF}. (e.v.)	Number of iterations
−9711·2623	−9711·2622	0
−9735·8160	−9708·3375	1
−9736·9326	−9708·2163	2
−9737·1415	−9690·7878	3
−9737·2188	−9674·2634	4
−9737·2503	−9664·2167	5
−9737·2638	−9585·8358	6
−9737·2707	−9630·9317	7
−9737·2724	−9577·9926	8
−9727·2736	−9628·7069	9
−9727·2741	−9577·5636	10
−9727·2743	−9628·5878	11
−9727·2745	−9577·5406	12
−9727·2745	−9628·5814	13
	−9577·5394	14

(2) One general observation made in course of our work is that for small values of the shifting parameters, the stationary points reached on the energy surface are quite stable and independent of shifter values. But for large values of these parameters, say 40 eVs or larger (such large values have to be used

frequently), convergence becomes slow and sometimes divergence sets in. To correct for this, we are now using modified level-shifted Hamiltonians F_α and F_β which converge to the unshifted Hamiltonians F_α^0 and F_β^0 in the limit of large number of iterations, thereby ensuring the stability of the solution obtained. Explicitly written,

$$F_\alpha^n = F^0{}_\alpha + \frac{1}{2^{n-m}}(I-P_\alpha^n)+b_\alpha(I-P_\alpha^n)$$

$$F_\beta^n = F_\beta^0 + \frac{1}{2^{n-m}}(I-P^n)+b_\beta(I-P_\beta^n)$$

where m is a small number (0 to 3) and n indicates the number of iteration being done currently. The details of calculation by this technique as also by a reversed level-shifting technique in which the occupied sub-space is shifted upward will be published shortly.

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